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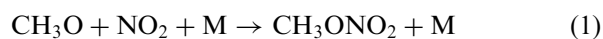
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Letter to the Editor

Reply to “Comment on ‘Long-term atmospheric measurements of C₁–C₅ alkyl nitrates in the Pearl River Delta region of southeast China’”

A recent modeling study by Archibald et al. (2007) verifies our understanding of the processes that form methyl nitrate (CH₃ONO₂) under polluted conditions.

Whereas oceans are the major global source of CH₃ONO₂ (Blake et al., 2003), Simpson et al. (2006) observed elevated levels of CH₃ONO₂ in the Hong Kong area that were not consistent with oceanic emissions. The enhancements could not be explained by photochemical production from the oxidation of methyl nitrate's parent hydrocarbon, methane (CH₄), nor by the decomposition of larger alkoxy radicals. Whereas the reaction:



is normally a minor formation pathway for alkyl nitrates, Flocke et al. (1998a, b) had postulated that a possible exception may be the formation of CH₃ONO₂ under very polluted conditions. As a result, Simpson et al. performed rough calculations using their Hong Kong data to show that this reaction likely occurs in polluted cities, but they suggested detailed modeling work to more fully verify the reaction's plausibility.

Based on box model calculations using European emission profiles of nitrogen oxides (NO_x) and volatile organic carbons (VOCs), Archibald et al. have confirmed that the mechanism described by Eq. (1) occurs under polluted conditions. Under the conditions specified in their model, they have shown that this reaction becomes important at 10 ppbv NO₂ and dominant at 35 ppbv NO₂. These abundances are consistent with levels that can occur in cities, and are sufficient to explain the enhancements that were observed in Hong Kong (as high as 25 pptv CH₃ONO₂, or about 20 pptv in excess of background values). As noted by Archibald et al., these model simulations are representative of

European rather than Asian emission profiles. Because the European VOC/NO_x mix will be very different than the Asian mix, we point out that the crossover point at which Eq. (1) becomes dominant may occur at a very different level of NO₂ in pollution from China.

It is also worth considering why the yield of CH₃ONO₂ via the reaction:



is shown to decrease with increasing NO₂. The hydroxyl radical (OH) will be suppressed at high NO₂, which reduces the production of CH₃O₂ and also increases the relative production of CH₃ONO₂ from Eq. (1), because the latter reaction competes with O₂ and is therefore essentially linear with NO₂.

In addition to Eq. (1), the liquid phase acid-catalyzed reaction of methanol (CH₃OH) with nitric acid (HNO₃) was also postulated in Simpson et al. as a possible mechanism to explain the elevated CH₃ONO₂ levels. However, a detailed analysis by Iraci et al. (2007) shows that the acidities of the particles are likely to be insufficient to reach the reaction rates required to generate even a fraction of the CH₃ONO₂ that was observed by Simpson et al. Therefore, the mechanism proposed by Flocke et al. (1998a, b) and verified by Archibald et al. provide the most complete understanding to date of the processes that are able to form CH₃ONO₂ in cities.

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